

# PATENT SPECIFICATION

746,864



Date of Application and filing Complete Specification Sept. 16, 1953.

No. 25656/53.

Application made in United States of America on Oct. 14, 1952.

Complete Specification Published March 21, 1956.

Index at acceptance :—Class 81(1), L4.

## COMPLETE SPECIFICATION

### Shampoo Compositions

We, COLGATE-PALMOLIVE-PETT COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America of 105 Hudson Street, Jersey City, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to shampoos.

According to the present invention a shampoo comprises a water-soluble organic synthetic detergent and a minor proportion in relation to the proportion of detergent of a substantially colourless hair-substantive organic fluorescent dye in an aqueous medium.

The shampoos of the invention are characterized by a high lathering or foaming power, excellent cleansing properties when applied to human hair in soft and hard water, and adsorption of the fluorescent dye upon the human hair with resultant elimination of dulling effects and added brilliance and lustre.

The synthetic detergent used in the present invention is preferably an anionic water-soluble organic sulphate or sulphonated detergent or a mixture of such detergents. The detergents preferably are aliphatic in structure. Among the suitable aliphatic detergents are sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g., "coconut" fatty acid monoglyceride monosulphate, and lauroyl monoglyceride and diglyceride monosulphate; the higher alkyl sulphates, including both primary and secondary higher fatty alcohol sulphates, e.g., lauryl sulphate, and mixed higher fatty alcohol sulphates derived from reduced coconut oil fatty acids; the higher fatty acids (e.g., coconut fatty acids) ethanolamide sulphates the higher fatty acid amides of amino lower alkyl sulphonc acids, e.g., lauric acid amide of taurine; and dioctyl sulphosuccinate. The terms higher fatty acid, and higher fatty alcohol are used herein to refer to acids or alcohols having an aliphatic chain of not less than eight carbon atoms, whilst the corresponding terms lower fatty acid and lower fatty

alcohol refer to compounds having a chain 50 with fewer carbon atoms. These aliphatic detergents preferably have an aliphatic chain within the range of 8 to 22 carbon atoms, whilst the carboxylic ester detergents preferably have an acyl radical of 8 to 18 carbon 55 atoms. The alkyl aryl sulphonate detergents may be employed, although these are less suitable because of their marked drying power. Alkyl aryl sulphonate detergents which may be used include those derived from 60 benzene, toluene, phenol and naphthalene, with the alkyl substituent selected for effective detergent power. Of the alkyl aryl sulphonates, it is preferred to use the higher alkyl benzene sulphonates wherein the alkyl group has 8 to 65 18, and preferably 10 to 16 carbon atoms, such as dodecyl benzene sulphonate or decyl benzene sulphonate.

These various anionic detergents are usually used in the form of their water-soluble salts. 70 The alkali metal salts, e.g., sodium, potassium or lithium, may be employed, though it is preferred to use the salts of nitrogen-containing bases, particularly in liquid shampoo solutions in view of the generally greater water-solubility of these salts. Suitable salts are the ammonium and lower alkylamine salts, such as the ethanolamine salts including mono-, di-, and triethanolamine salts, and mixtures thereof. 80

With regard to the fluorescent dye, it may be mentioned that a development in the textile industry has been the incorporation into laundering compositions of certain fluorescent chemical compounds for the purpose of making 85 laundered fabrics appear whiter. These so-called whitening agents or optical bleaches are fluorescent dyes which, when applied to cellulosic fibres, absorb ultraviolet light and emit visible light. By fluorescing blue to the ultraviolet rays in daylight, such dyes offset to some degree the yellowing tendencies developed in many white fabrics. Florescent dyes have also been suggested for other applications, such as for use in paper products, as sun-screening 95 agents in sun-tan lotions, and as identification markings.

The formulation of shampoos, however, is

[Price 3s. 0d.]

Price 4s. 6d.

Price 2s. 6d.

a specialized field of endeavor and many special considerations have to be taken into account such as cleaning power, rinsability, and absorption effects on the hair, as well as the requisite physical and chemical properties of the products, e.g., adequate concentration of solids, and compatibility of the ingredients. Thus for the purpose of the present invention there are certain special criteria of suitability for the fluorescent dye which should be observed.

The fluorescent dyes suitable for use in the present invention should possess the following properties. First, the dyes should absorb the near ultra-violet rays such as from about three thousand up to about four thousand Angstrom units and emit light in the visible range. Secondly, the emitted visible light should be substantially colourless (this does not exclude a blue or violet tinge in the emitted light, as distinguished from a deep colour), which tends to accentuate the hue of the hair and reduce dulling effects, particularly on blonde or grey hair. Furthermore, the fluorescent dye should not basically change the original or desired colour of the shampoo, in the quantities in which it is normally employed. Another requirement is that the dye should be sufficiently substantive or adsorbed upon human hair while in contact with the detergent and under the conditions of use, since a dye that is substantially non-substantive to hair cannot give the desired effects. This requirement involves a number of considerations. It has been found that hair-substantive dyes are amenable to selective adsorption by the hair from solutions containing the indicated sulphated or sulphonated detergents during the cleansing procedure and will not be readily washed off during the rinsing or other subsequent cleaning operations. The anionic detergent *per se* is usually substantive to hair also, but the fluorescent dye is preferentially or selectively adsorbed during use of the shampoo. The term "adsorption" is used herein to denote that the dye is retained upon the hair and there exhibits the fluorescent effect. The exact mechanism of the action, whether it be absorption, adsorption, electrostatic or hydrogen bonding, or some other effect, is not known at this time. Another requirement is that the fluorescent dye should be uniformly dispersed in the aqueous medium in order to facilitate proper application. The dye may be dissolved, emulsified or similarly incorporated in the shampoo, depending upon the particular composition and type of product. Further considerations include non-toxicity and non-irritability under conditions of use.

It has been found that suitable dyes having superior hair-substantivity are the fluorescent coumarin compounds, particularly the hair-substantive 4-methyl coumarin compounds. Optimum effects have been obtained with the use of 4-methyl, 7-diethyl amino coumarin, though other 4-methyl, 7-di lower alkyl amino

coumarin compounds such as 4-methyl, 7-dimethyl amino coumarin may be employed with satisfactory results. Another suitable compound is 5,7 dihydroxy 4-methyl coumarin.

These dyes exhibit more pronounced affinity for the hair in the presence of the detergent when the shampoo is somewhat acid, such as having a pH from 4 up to 7, and usually in the range 4.5—6.5. Such effects are characteristic with these dyes, since other types of dyes may exhibit their optimum effect in alkaline solution. This characteristic of the coumarin compounds can be fully exploited in shampoo containing sulphated or sulphonated detergents since these detergents exhibit effective cleaning and foaming power under acid conditions. Furthermore, it is preferred to employ the aliphatic carboxylic ester detergents, such as fatty acid monoglyceride sulphates, in an acidic medium, since these detergents are more liable to hydrolysis or decomposition when alkaline. The acidity of the shampoo may be adjusted in any suitable manner, such as by the addition of mineral acids, e.g. sulphuric acid, to the detergent. Suitable organic acids such as citric acid may be used also. Bases such as ammonium hydroxide may also be used as desired for correcting over-acidity.

The indicated coumarin dyes are water-insoluble for practical purposes, but the detergent aids in the apparent solubilization of these dyes in an aqueous medium, and it is thus possible to produce clear, homogeneous liquid shampoos containing these coumarin dyes. Such dyes usually are mildly cationic in nature, but they do exist in apparent solution with the anionic detergent in the proportions employed in shampoos.

With regard to the proportions of detergent and fluorescent dye in the shampoo in general the concentration of the detergent should be at least 5%, e.g., within the range of 5—50%, and usually within the range 10—35%, though it is preferred to use from 15 to 30% detergent, by weight of the shampoo. Such detergent concentrations will be sufficient to cleanse the hair effectively and ensure adequate foaming or lathering power. The foaming property is beneficial, since the foam or lather aids in dispersing or bringing the dye into thorough contact with the hair, thereby effecting more uniform adsorption. These proportions are also in excess of the critical micelle concentration of the sulphated or sulphonated detergents, which increases the solubilization of the fluorescent dyes in the aqueous medium. In clear liquid shampoos, the amount of detergent should, of course, be within its solubility limits in the solvent. The fluorescent dye is employed in minor proportion in relation to the proportion of detergent and in a sufficient amount for preferential adsorption upon the hair, but does not exceed 1% by weight of the shampoo composition. It has been found that, generally at least 0.05% is required, but

it is preferred to use at least 0.1% of the dye by weight of the shampoo; excellent results are obtained with concentrations of at least 0.2%

- 5 The solubilization effect on the fluorescent dye exerted by the detergent can be enhanced by adding a water-soluble (including water-miscible) alcoholic solvent. The lower monohydric alcohol solvents such as ethyl alcohol and isopropyl alcohol are particularly useful in the formulation of clear liquid shampoos, both for solubilizing the fluorescent dye and for stabilizing the shampoo under adverse conditions. Other alcohols such as propylene glycol and methyl carbitol may be employed if desired. Such alcoholic solvents should, ordinarily, be used in minor amounts, such as from 1—30% and preferably 5—25% by weight of the shampoo. The aqueous (including aqueous alcoholic) medium preferably forms the major proportion of the total composition, being at least 50%, and preferably from 65% up to 95% by weight of the shampoo.

- 25 In addition to clear liquid shampoos, the shampoo compositions of the present invention may be prepared in any desired physical form, including liquid creams, pastes, gels, and aerosol shampoos. Such products may be prepared in the usual manner. The fluorescent dye is usually incorporated with the detergent in the aqueous base with stirring under slightly elevated temperatures, such as about 65° C. Any desired additional ingredients may be incorporated in the conventional manner.

- It is common to add various adjuvant materials to shampoo compositions. Such additional ingredients may be employed as desired, depending, of course, upon the desired character of the final product. Thus, the shampoo ordinarily will contain perfume which should be selected so as to be compatible with the other ingredients. Suitable buffering materials may also be added as desired. Other ingredients which may be used in shampoos for imparting desired qualities to the hair or the product are hair conditioners of superfatting materials such as lanolin, lecithin, fatty alcohols or fatty amides, in minor proportions. Minor amounts of inorganic salts such as ammonium sulphate, triethanolamine sulphate or sodium pyrophosphate may be present in the shampoos also. Glycerine may also be added, in amounts up to 10% usually. Colouring materials, such as dyes or whitening agents for the shampoo may also be employed as desired. Preservatives such as sodium benzoate may be added to prevent mould growth. Thickening agents such as sodium carboxymethylcellulose may also be used.

- 65 The invention may be performed in various ways, and the following specific examples are given by way of illustration. The percentages of the various ingredients are by weight.

#### EXAMPLE I

The following composition was a clear homogeneous liquid shampoo:—

|   | %    |    |
|---|------|----|
| *Detergent salt - - - - -                   | 21.0 | 70 |
| 4-methyl 7-diethyl amino coumarin - - - - - | 0.2  |    |
| Ethyl alcohol - - - - -                     | 9.3  |    |
| Perfume - - - - -                           | 0.4  |    |
| Water - - - - -                             | Q.S. | 75 |

\*—Ammonium salt of sulphated monoglyceride of coconut oil fatty acids.

It contained about 10% by weight of inorganic sulphate salt formed in its manufacture.

This composition had a pH adjusted to about 6.2. Upon use on the hair, this shampoo exhibited a high level of lathering and cleansing power with marked adsorption of the fluorescent material upon the hair. The hair after washing had a greater lustre and sheen than was obtained with shampoos which did not contain such fluorescent dye.

#### EXAMPLE II

Another satisfactory clear liquid shampoo had the following composition:—

|   | %    |    |
|---|------|----|
| *Detergent salt - - - - -                   | 25.0 |    |
| 4-methyl 7-diethyl amino coumarin - - - - - | 0.2  | 95 |
| Water - - - - -                             | Q.S. |    |

\*—Triethanolamine lauryl sulphate. The composition was adjusted to a pH of about 6.

#### EXAMPLE III

The following composition was a satisfactory liquid cream shampoo:—

|   | %    |     |
|---|------|-----|
| *Detergent salt - - - - -                   | 20.0 |     |
| 4-methyl 7-diethyl amino coumarin - - - - - | 0.2  | 105 |
| Stearic acid - - - - -                      | 3.0  |     |
| Triethanolamine - - - - -                   | 1.3  |     |
| Lanolin - - - - -                           | 0.5  |     |
| Perfume - - - - -                           | 0.4  |     |
| Water - - - - -                             | Q.S. | 110 |

\*—Sodium salt of sulphated monoglyceride hydrogenated coconut oil fatty acids. It contained 10% by weight of sodium sulphate. The composition had a pH adjusted to about 6.

What we claim is:—

1. A shampoo comprising a water-soluble organic synthetic detergent and a minor proportion in relation to the proportion of detergent of a substantially colourless hair-substantive organic fluorescent dye, in an aqueous medium.
2. A shampoo as claimed in Claim 1 in which the fluorescent dye is a coumarin compound.
3. A shampoo as claimed in Claim 1 in which

the fluorescent dye is a 4-methyl 7-di lower alkyl amino coumarin.

4. A shampoo as claimed in Claim 1 in which the fluorescent dye is 4-methyl 7-diethylamino 5 coumarin.

5. A shampoo as claimed in any of the preceding claims in which the fluorescent dye is present in sufficient amount for preferential adsorption upon hair but does not exceed 1% 10 by weight of the shampoo.

6. A shampoo as claimed in any of the preceding claims in which the detergent is an anionic sulphated or sulphonated detergent.

7. A shampoo as claimed in any of Claims 1 15 to 5 in which the detergent is a higher fatty acid monoglyceride sulphate.

8. A shampoo as claimed in any of Claims 1 to 5 in which the detergent is a higher alkyl sulphate.

20 9. A shampoo as claimed in any of the preceding claims in which the detergent is in the

form of a salt of a nitrogen containing base.

10. A shampoo as claimed in any of Claims 1 to 8 in which the detergent is in the form 25 of an ammonium salt.

11. A shampoo as claimed in any of the preceding claims in which the amount of the detergent present is between 10% and 35% by weight of the shampoo.

12. A shampoo as claimed in any of the preceding claims in which the aqueous medium is 30 an alcoholic aqueous medium.

13. A shampoo as claimed in any of the preceding claims which is acidic.

14. A shampoo as claimed in any of Claims 1 35 to 12 of which the pH value is between 4.5 and 6.5.

15. A shampoo having a composition substantially in accordance with any of the foregoing 40 examples.

KILBURN & STRODE,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1956.  
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.